

PATENT SPECIFICATION

NO DRAWINGS

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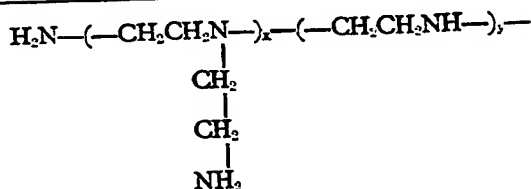
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COMPLETE SPECIFICATION

Improvements in Writing Inks

- We, CLARENCE SCHREUR and GORDON SMISER LACY, both citizens of the United States of America, trading as PACIFIC RESEARCH LABORATORY, of 529 West Fourth Street, Escondido, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to inks for writing or marking cellulosic materials and more particularly deals with what are known as writing inks.
- Inks of this type generally fall into two types. So-called permanent inks are formed of an iron salt and gallotannic or tannic acid, usually with a dyestuff to afford strength of colour during the writing operation. This ink sets up in the fibres of the paper in a few days and thereafter is fairly resistant to moisture and light. Such inks are highly acidic and tend to corrode all pen nibs save those of precious metals.
- Other writing inks are generally referred to as washable and usually consist of a solution of soluble dyestuff. These may usually be washed from clothing without difficulty; likewise, when water is applied to paper marked with such inks it runs badly.
- There have recently been offered to the public devices commonly known as felt tip marking pens where the ink feeding device is either felt or some equivalent porous medium. The inks are most frequently solutions of dyestuffs in organic solvents. Such solvents are frequently flammable and may even be toxic. As they are usually highly volatile, the writing instrument must be kept
- tightly capped when not in use. Inks having an aqueous solvent base are either completely washable or bleed badly when wet. There is not available on the market today a dyestuff-water base ink that is impervious to water after being applied to a cellulosic material and allowed to dry.
- It has now been found that an alkaline solution of polyethyleneimine resin and a suitable dyestuff produces a highly desirable writing ink for application to cellulosic substances. After drying, the marks produced are practically impervious to water and all common solvents. Some eradication may be accomplished by the use of aqueous alkaline solutions.
- The most suitable dyestuffs are the direct dyestuffs and many of the acid dyestuffs. As the light-fastness of the dyestuff is not materially improved, this inherent quality of the dyestuff must be taken into account in its choice. Among the dyestuffs found useful are: Chlorantine Fast Red 5B, Syno Direct Fast Red 8 BLNW, Phloxine BP, Pontamine Fast Orange EGL, Chlorantine Fast Yellow 5GLL, Chinoline Yellow SSF, Direct Brilliant Green CBM, Fastazol Turquoise Blue LGP, Luxol Fast Blue MBSN, Pontamine Fast Violet 4BL, Calcodur Violet 4BL, Pontamine Fast Brown NP, Direct Black E, Calcomine Black BHD and Pontamine Black ULR.
- The polyethyleneimines may have a molecular weight in excess of 500 extending upwardly to about 100,000. The molecules are highly branched with a wide distribution among primary, secondary and tertiary amines, and may be generally represented by the formula:



The products are available as hygroscopic, amorphous substances or in aqueous solution. The material has been characterised as a cationic flocculating agent, highly substantive to cellulosic fibres.

Water which should preferably be distilled or deionised, may suitably be used as the solvent in the inks of the invention, but a heavier, less volatile organic solvent may be used instead of, or in addition to, water for applications such as stamp pad and recorder inks. Suitable organic solvents are polyhydric alcohols and their ethers. Preferred organic solvents are glycerine, the glycols and the glycol ethers. The viscosity may be further adjusted by such agents as polyvinyl pyrrolidone. The use of a trace of antiseptic or bactericide is followed as is common in the trade; phenol or one of the substituted or poly phenols is suitable. To adjust the pH within desired limits, an inorganic basic material, i.e. ammonia, or an organic amine, such as one of the ethanolamines, may be used. The organic amine should be water soluble, if water is the solvent. If the product is too alkaline, an organic acid such as acetic acid, is used to adjust the pH.

The invention is illustrated by the following examples, in which "PEI" stands for "polyethyleneimine" and parts are parts by weight.

EXAMPLE 1

	Parts
Direct Black E	6
PEI Resin	3
Water	91
pH	11

The dyestuff is dissolved at room temperature in water and the pH adjusted to 9 with ammonia. To this is added the PEI of 1,200 M.W. as a 33% solids aqueous solution. Other dyestuffs may be substituted in varying amounts from 0.05 to 12.0% by weight of the ink. The resin may be used in an amount from 0.05 to 10% by weight of the ink and the pH range is 10.5 to 12.5. The resulting ink may be used in a fountain pen or a felt tip marking pen. When applied to paper, as

the mark dries, it is permanent.

The same procedure was followed in preparing inks of the formulations set out in the following examples—

EXAMPLE 2

	Parts	
Chinoline Yellow SSF	2	55
PEI, M.W. 600	3	
Water	95	
pH	11	

EXAMPLE 3

	Parts	
Direct Brilliant Green CBM	5	60
PEI, M.W. 1,800	5	
Water	90	
pH	11	65

EXAMPLE 4

	Parts	
Chlorantine Fast Yellow 5GLL	0.25	
PEI, M.W. 1,000—5,000	3	
Water	96.75	70
pH	11.5	

EXAMPLE 5

	Parts	
Fastusol Turquoise Blue LGP	5	
PEI, M.W. 40,000—60,000	3	75
Water	92	
pH	11.5	

EXAMPLE 6

	Parts	
Pontamine Fast Violet 4BL	2	80
PEI, M.W. 50,000—100,000	3	
Water	95	
pH	11	

EXAMPLE 7

	Parts	
Phloxine BP	1	85
PEI, M.W. 1,800	0.5	
Glycerine	59	
Water	39.5	
pH	10	90

This ink is suitable for both capillary and stamp pad use.

EXAMPLE 8

	Parts	
Calcodur Violet 4BL	2	95
PEI, M.W. 1,800	3	
Glycerine	49	
Carbitol	4	
Water	42	
pH	11	100

This ink is suitable for stamp pad use.

EXAMPLE 9

	Luxol Fast Blue MBSN	Parts
	PEI, M.W. 1,200	31
	Propylene glycol	4
5	Monoethanol amine	48
	Polyvinyl pyrrolidone	10
	pH	7
		10.5

This ball pen ink is prepared by heating for a period of one to four hours at a temperature range of 70° to 90°C. followed by filtration, preferably at the temperature to which the mixture is heated. If adjustment is made for acidity, the pH can be raised by using an organic amine soluble in the vehicle system and the pH can be lowered by using a suitable organic acid such as acetic acid or a fatty acid.

It will be understood that the parts by weight set forth in each of the foregoing specific examples of formulations typical of those coming within the purview of this invention and distributed generally over the range of PEI molecular weights found suitable are the proportions generally preferred. However, these proportions of the principal ingredients may be varied. Generally speaking, the range of dyestuffs used depends upon the intensity of the mark desired and the solubility of the particular dyestuff employed. The ranges given in the first specific example are generally illustrative and will enable a person skilled in this art to employ variants in the proportions of the ingredients best satisfying the results desired in a particular end use of a formulation. Each dyestuff has its own inherent and characteristic alkalinity and this is taken into account by the skilled person in this art in varying the pH range generally within the range set forth in the first specific example when preparing formulations using other dyestuffs and PEI having a molecular weight from 500 to 100,000.

From the foregoing, it will be apparent that the polyethyleneimines are most effective in ink formulations.

WHAT WE CLAIM IS:—

1. A writing ink comprising an alkaline solution of a polyethyleneimine and a dyestuff.
2. An ink according to claim 1, wherein the solvent is water. 50
3. An ink according to claim 1, wherein the solvent is an organic solvent.
4. An ink according to claim 3, wherein the organic solvent is selected from polyhydric alcohols and their ethers. 55
5. An ink according to claim 1, wherein the solvent comprises water and an organic solvent selected from polyhydric alcohols and their ethers. 60
6. An ink according to claim 4, wherein the organic solvent is glycerine, a glycol or a glycol ether.
7. An ink according to claim 5, wherein the organic solvent is glycerine, a glycol or a glycol ether. 65
8. An ink according to claim 2, claim 5, or claim 7, wherein the water is distilled or de-ionised water.
9. An ink according to any one of the preceding claims wherein the dyestuff is selected from acid and direct dyestuffs. 70
10. An ink according to any one of the preceding claims wherein the molecular weight of the polyethyleneimine is between 500 and 100,000. 75
11. An ink according to any one of the preceding claims wherein the contents by weight of dyestuff and polyethyleneimine are respectively from 0.05 to 12% by weight and 0.05 to 10% by weight. 80
12. An ink according to any one of the preceding claims having a pH value of from 10.5 to 12.5.
13. An ink according to any one of the preceding claims wherein the alkalinity is supplied by ammonia or an organic amine. 85
14. A writing ink substantially as herein described and exemplified.

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